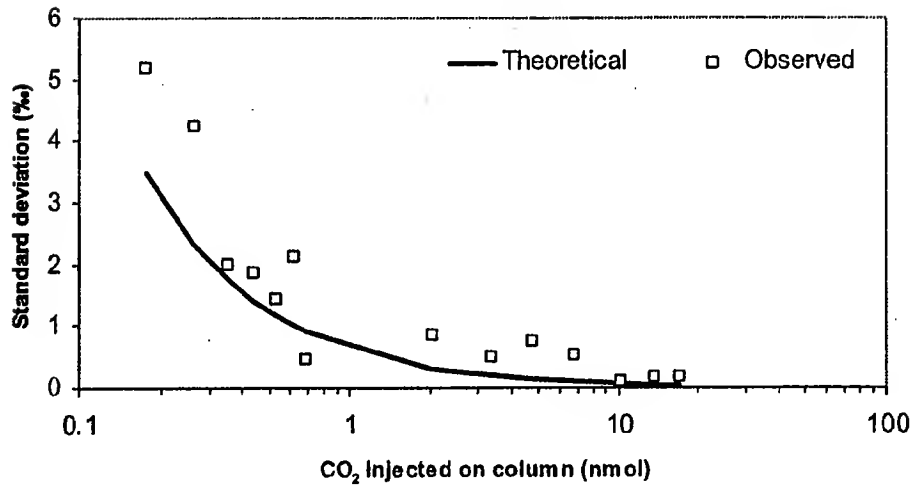

Fig. 6. S.D.($\delta^{13}C_{pdb}$) vs. CO_2 injected on column for simulated 16-bit data. The line indicates the theoretical limit of precision as a function of injection size, as calculated from Eq. (12).

At natural abundance, a standard deviation of $\sigma_{ppt} = 1.0$ is approximately equivalent to S.D.($\delta^{13}C_{pdb}$) = 1.0‰. We used Eq. (12) to predict the standard deviation as a function of injection size at 16-bit resolution, compensating for an open split ratio of 8.4:1. The integration window, W, was assumed to be constant at 10 s, $E = 5000$, and $R_\Omega = 3 \times 10^8\ \Omega$. A plot of the calculated limits compared to the observed precision at 16 bits is shown in Fig. 6. There is good agreement between theory and experiment. The calculated precision is within a factor of five of the observed precision for all injection sizes. More striking, the calculated precision is a "lower limit", as nearly all the measured precisions lie above the theoretical prediction. The biggest discrepancies occur for large injection sizes, where the effect of quantization error is minimized, and other sources of error (e.g. contaminants) may dominate.

Eq. (12) can also be used to demonstrate that quantization error should be negligible for signals acquired with 24-bit digitizers. Eq. (12) predicts that only 0.6 pmol of CO_2 to the IRMS should be necessary to achieve a precision of 0.5‰ if quantization error is the only limiting factor. However, counting statistics dictate that a minimum number of ions must be formed to achieve a specified precision to overcome the shot-noise limit. Merritt and Hayes [11] give this equation as:

$$\sigma_\delta^2 = \frac{(2 \times 10^6)(1+R)^2}{EmN_a R} \quad (13)$$

where σ_δ is the shot noise limited standard deviation, R is the natural abundance isotope ratio, E is the ionization efficiency, m is the moles of CO_2, and N_a is Avogadro's number. Substituting $E = 5000$ and $R = 0.011$, we find that 6 pmol of analyte is required to achieve S.D. < 0.5‰. Therefore, when high precision 24-bit boards are used, the effect of quantization error is superseded by shot noise.

Our theoretical treatment gives insight into why curve-fitting is less sensitive to quantization error than summation. In the summation methods we have discussed, imprecision in a single data point chosen as the background is multiplied throughout the background correction; for a peak width of N data points, the total quantization error scales as N. In contrast, the algorithms used in curve-fitting minimize the sum of squares between the fit curve and *every* data point. In curve-fitting, the quantization noise for each individual point is averaged over the entire curve; for N data points, the total quantization error scales as $N^{1/2}$. For a peak width of 10 s and a sampling rate of 10 Hz, this translates into a 10-fold reduction of quantization error.

The theoretical treatment we describe is appropriate for understanding the effects of quantization error on summation integration methods that choose single points on either side of the peak to define a background. It does not examine the limits of other classes of data reduction methods. An obvious improvement to the summation integration method would be to average n points on either side of the peak, which would increase the effective number of bits of

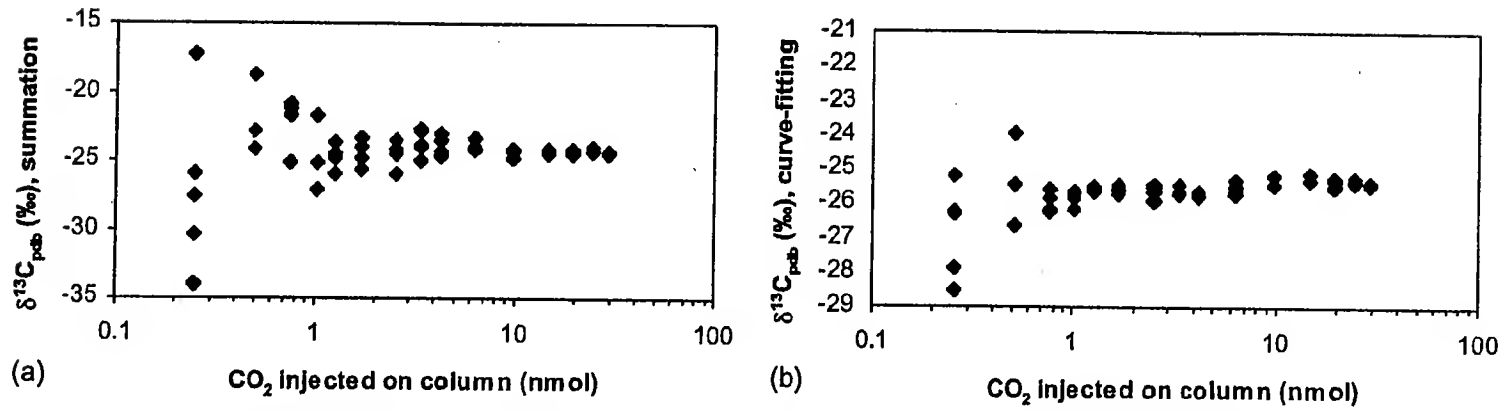

Fig. 7. $\delta^{13}C_{pdb}$ vs. CO_2 injected on column for (a) individual summation and (b) curve-fitting algorithms. Data was collected at 16 bits and 10 Hz on the APP2003.

the background measurement by $n^{1/2}$. While this approach could work well for isothermal runs with constant background, it is much less suitable for complex GC–CIRMS chromatograms, where it is not obvious *which* points should be averaged; that is, which points represent pure background and do not contain chemical noise or the tail ends of peaks. Ricci et al., observed that the averaging method gives slightly higher background values then other corrections [3]. They also reported that the dynamic background correction (which uses single points) yielded improved δ-values over the averaging method. Thus, a method may be insensitive to quantization error, but may still give worse results due to other variables.

3.3. Improving precision on a 16-bit IRMS

To test the effectiveness of curve-fitting on GC–CIRMS data acquired by low precision digitizers, we ran multiple CO_2 injections on an APP2003 using 16-bit digitizers, and otherwise in similar fashion to the work on the FMAT252. A plot of $\delta^{13}C_{pdb}$ versus injection size is shown for summation (Fig. 7a) and curve-fitting (Fig. 7b). Fig. 8 shows a plot of S.D.($\delta^{13}C_{pdb}$) as a function of injection size for both integration methods. The theoretical limit on the summation method, calculated from Eq. (12), is shown in the same figure as a dashed line. The observed precision for the summation method agrees well with theoretical predictions; most of the data points lie just above the lower limit curve. Almost 15 nmol of CO_2 on column are necessary to achieve a precision of <0.3% using the summation method. Using curve-fitting, only 0.76 nmol are necessary to reach that level of precision, a 20-fold improvement. This is greater than the two-fold advantage seen by curve-fitting the 16-bit data from the FMAT 252. One possible explanation is that the APP2003 data is

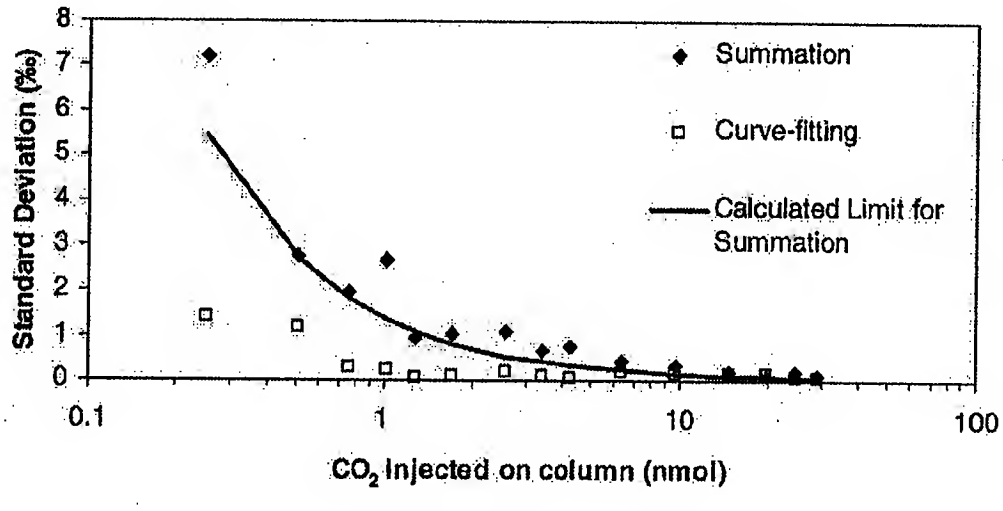

Fig. 8. S.D.($\delta^{13}C_{pdb}$) vs. CO_2 injected on column for runs on APP2003 with 16-bit boards. The dashed line indicates the theoretical limit of quantization error on precision as a function of injection size, as calculated from Eq. (12).

affected primarily by bit noise, while the FMAT252 data has other sources of noise that cannot be eliminated by curve-fitting. The FMAT252 accepts a three-fold higher flow rate than the APP2003, so there is likely more chemical noise in the FMAT252 signal.

The relative immunity to quantization error with curve-fitting permits the IRMS to be run at lower inlet flow rates, which effectively increases quantization noise by decreasing the number of steps between background and peak with relatively little influence on chemical noise. The advantages of lower inlet flow rates are a longer lifetime for the filament, and reduced need for pumps and pumping capacity. These benefits, plus the reduced need for expensive ADC boards, should make high-precision GC–CIRMS more amenable to portable and low-cost applications. In principle, statistical considerations define the lower limits of flow rates. However, counting statistics dictate that S.D. = 0.5‰ requires 6 pmol of CO_2 to the source for a typical continuous flow IRMS ($E = 5000$), and GC–CIRMS applications usually work well above this limit. Thus, modestly lower resolution and inlet flow rates should not significantly affect performance, so long as appropriate integration techniques are used.

4. Conclusions

Data reduction using curve-fitting is more robust than the conventional summation method in the presence of even modest levels of quantization error. Using data obtained on high precision digitizers, the curve-fitting algorithm required several-fold less CO_2 to reach benchmarks of high precision (S.D. = 0.3, 0.6, and 1.0‰) at any of the three simulated board depths (12, 14, or 16 bits). The poor performance of the summation algorithm was particularly noticeable at the 12-bit resolution, where S.D. <1.0‰ could not be reached even at the maximum injection size allowed by the dynamic range of the Faraday cups. We have derived an expression that describes the influence of quantization noise on isotope ratios calculated from raw IRMS data, and shown that it accurately predicts the lower limit of precision. Our theoretical treatment assumes that quantization error is uncorrelated between the $m/z = 44$ and 45 signals, and is appropriate for any data reduction algorithm that uses single points on either side of the peak to describe the background.

Curve-fitting substantially improved precision on GC–CIRMS data collected by an instrument with 16-bit digitizers. The summation algorithm required 15 nmol of CO_2 on-column to achieve a precision of S.D. = 0.3‰, while curve-fitting required only 0.76 nmol. Thus, IRMS with 16-bit ADC boards achieved high precision for less than 1 nmol of C on column, a common benchmark for GC–CIRMS applications, despite using 16-bit ADC boards. Lower inlet flow rates, enabling reduced pumping requirements, may be an important advantage in some applications.

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